Metal-insulator transition in $La_{0.7}Sr_{0.3}Mn_{1-x}Fe_xO_3$

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We report the effect of Fe doping at the Mn site in $La_{0.7}Sr_{0.3}MnO_3$ oxides. We find that the doping of Fe does not cause any structural change, but the electrical transport in the system is strongly affected. The parent compound $La_{0.7}Sr_{0.3}MnO_3$ shows a resistivity peak at $T=T_p$ (365 K) and behaves as a ferromagnetic metal at low temperature. Double exchange (DE) interaction between Mn^{3+} and Mn^{4+} is understood to be the cause of ferromagnetism and metallicity of the material. As Fe is doped into the system a depletion in the number of hopping electrons occurs and consequently the DE interaction becomes weak, however, as long as $x\leqslant 0.2$ the system shows metallic behavior at low temperatures. For higher Fe doping the system becomes insulating throughout the whole temperature range. Electron tunneling conductance measurements show that the density of states of metallic samples exhibits a dip at E_F. As the value of x increases the dip deepens and finally at $x=0.25$ a gap opens up at the Fermi level. © *1999 American Institute of Physics.* [S0021-8979(99)10020-3]

I. INTRODUCTION

During the last few years perovskite manganese oxides $La_{1-y}A_yMnO_3$ (A: Sr, Ba, Ca) have attracted worldwide scientific attention.[1–6] This is because of their technological importance and unusual magnetic and transport properties, particularly the phenomenon of giant magnetoresistance. The typical composition[4,5] where this effect is most prominent is $y=0.3$. These compounds are characterized by a ferromagnetic-paramagnetic transition at T_c and a resistivity peak at T_p, $T_c\approx T_p$. Conventionally the *double exchange interaction* model[7] is used to explain the electrical and magnetic properties of these compounds. But recently Millis, Shraiman, and Mueller[8] have shown that double exchange alone cannot account for the behavior of the system and suggested that in addition to that a strong electron-phonon interaction arising from the lattice distortion associated with the Jahn–Teller (JT) splitting of the Mn d level plays a crucial role.

In the past a lot of work has been done to understand the nature of these materials. Most of these studies were done by replacing La by other rare earth elements. There are very few studies[9–11] where doping is done at the Mn site. We feel that the partial replacement of Mn, which plays a key role in the conduction process, by other transition metals may give important information about the nature of the system. For this purpose we doped Fe in $La_{0.7}Sr_{0.3}MnO_3$ and performed precise measurements of electrical resistivity and electron tunneling conductance measurements. Fe was chosen as the dopant because Mn^{3+} and Fe^{3+} have identical ionic sizes[11,12] and hence the crystal structure of the material remains unaltered.

II. EXPERIMENT

All the samples were prepared by the conventional solid state method. Appropriate amounts of La_2O_3, $SrCO_3$, Fe and MnO_2 were heated at 1250 K for 24 h. The reacted powder, obtained after heating, was pelletized and heated to 1250 K for 48 h. The resulting pellet was ground, repelletized and heated at 1300 K for 24 h. This procedure gave a sample with a very high packing density (≈90% of ideal density). The phase purity was checked by x-ray diffraction.

A four-probe ac technique[13] was employed to measure the electrical resistivity of all the samples in the temperature range of 2.5–370 K. A lock-in amplifier (Stanford Research Systems: SR830), a voltage to current convertor (homemade, driven by the lock-in sine out) and a temperature controller (Lake Shore Cryotronics: DRC-82C) were used. The absolute accuracy of resistivity is about 10% owing mainly to uncertainities in the geometrical factor; but the resolution was better than 1 part in 10^5.

The tunneling conductance measurements were carried out on tunnel junctions formed by pressing a small Pb piece (counter electrode) against the sample. Tunnel barrier is formed by the native oxide surface on Pb. A programmable current source (Keithley Model 220) and a nanovoltmeter (Keithley model 182) were used to obtain the $I-V$ characteristics of the junction. The differential conductance $G(V)$ was obtained numerically. All the measurements were performed at 1.2 K by dipping the samples in a pumped He^4 bath in a glass Dewar.

III. RESULTS AND DISCUSSION

X-ray diffraction pattern of the samples shows single phase systems. All the samples crystallize in cubic phase with the same lattice parameters ($a=7.760$ Å).

Electrical resistivity data of $La_{0.7}Sr_{0.3}Mn_{1-x}Fe_xO_3$ samples with $0\leqslant x\leqslant 0.25$ are shown in Fig. 1. In the undoped sample ($x=0$), ρ first increases with decrease in temperature, exhibits a peak at $T=T_p$ ($\approx T_c$) and then decreases as T is further reduced below T_p (see inset of Fig. 1). As Fe concentration increases the resistivity increases and T_p de-

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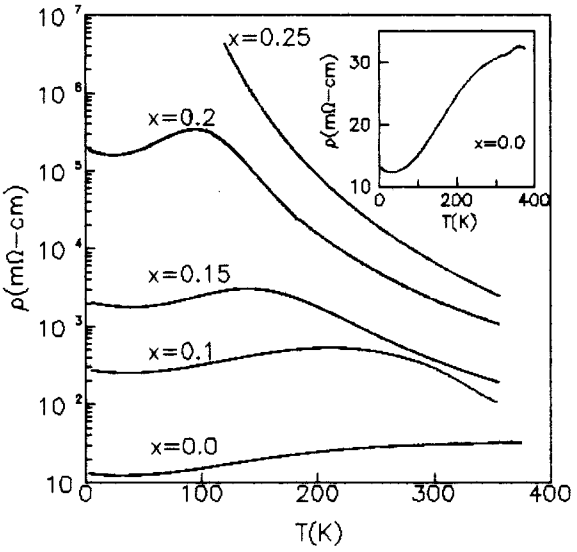

FIG. 1. Electrical resistivity of $La_{0.7}Sr_{0.3}Mn_{1-x}Fe_xO_3$ ($x \leqslant 0.25$). Inset shows the electrical resistivity of $La_{0.7}Sr_{0.3}MnO_3$ in an enlarged scale.

creases (see Table I). For $x \leqslant 0.2$ all the samples show a peak in ρ, characteristic of a metal-insulation (M-I) transition, and the samples are metallic at lower temperatures. The $x = 0.25$ sample shows insulating behavior throughout the whole temperature range.

The behavior of the system can be explained by considering the electronic band structure of the material. The configuration of d electrons in transition metal oxides is determined by the internal crystal fields. In an octahedral field, the d levels split into $t_{2g\uparrow}$, $e_{g\uparrow}$, $t_{2g\downarrow}$ and $e_{g\downarrow}$ as shown in Fig. 2(a). In solids these energy levels form bands. The electronic configuration for Mn^{3+} is $t^3_{2g\uparrow}\, e^1_{g\uparrow}$ and for Mn^{4+} it is $t^3_{2g\uparrow}$. In $La_{0.7}Sr_{0.3}MnO_3$, Mn exists both as Mn^{3+} as well as Mn^{4+}. So $t_{2g\uparrow}$ band is full and $e_{g\uparrow}$ band is less than half filled. The schematic band structure of $La_{0.7}Sr_{0.3}MnO_3$ can be represented as in Fig. 2(b). The $e_{g\uparrow}$ band of Mn is electronically active, where electron hopping occurs between Mn^{3+} and Mn^{4+}. Separation between $t_{2g\uparrow}$ and $e_{g\uparrow}$ has been estimated[14] to be $\approx$1.5 eV. The Fermi level lies $\approx$3.0 eV above the top of the $2p$ oxygen band.

Jonker[9] has studied the electrical conductivity of a Fe doped manganite, $La_{0.85}Ba_{0.15}Mn_{1-x}Fe_xO_3$, and showed that for $0 < x < 0.85$ the system has Fe^{3+}, Mn^{3+} and Mn^{4+} ions and for $0.85 < x < 1.00$ the system has Fe^{3+}, Fe^{4+} and Mn^{4+}

TABLE I. T_p and the fit parameters for the tunneling conductance data of $La_{0.7}Sr_{0.3}Mn_{1-x}Fe_xO_3$ ($x \leqslant 0.25$) to $G(V) = G_0[1 + (|V|/\Delta)^n]$. Data in the range 10 mV $< V <$ 100 mV were used for fitting. N is the number of data points used for fitting ($N \sim 100$).

x	T_p K	G_0 S	Δ (meV)	n	χ^2/N
0.0	365	0.0224(2)	401(17)	0.80(4)	1.9
0.1	210	0.0161(4)	127(3)	0.85(3)	2.8
0.15	140	0.0133(1)	161(4)	0.85(4)	5.1
0.20	95	0.0045(1)	152(3)	0.94(4)	3.5

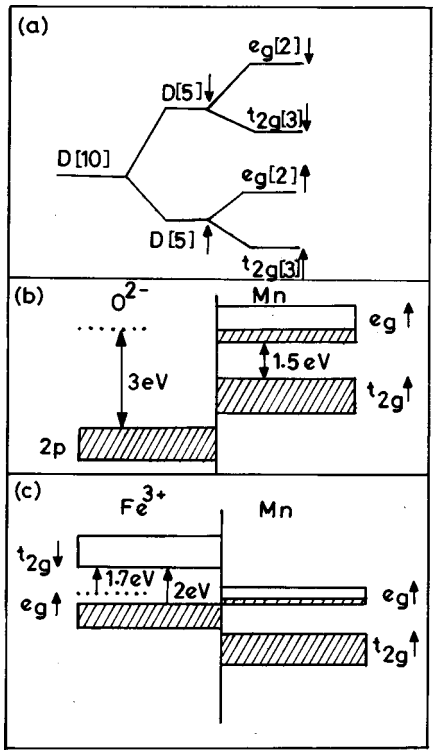

FIG. 2. (a) Octahedral field splitting of d levels, (b) schematic band structure of $La_{0.7}Sr_{0.3}MnO_3$, (c) band structure of Fe and Mn in $La_{0.7}Sr_{0.3}Mn_{1-x}Fe_xO_3$.

ions. The electronic configuration for Fe^{3+} is $t^3_{2g\uparrow}\, e^2_{g\uparrow}$ and for Fe^{4+} it is $t^3_{2g\uparrow} e^1_{g\uparrow}$. Simultaneous existence of Fe^{3+}, Mn^{3+} and Mn^{4+} indicates that the Fe $e_{g\uparrow}$ band is full and the Mn $e_{g\uparrow}$ band is less than half filled. While the existence of Fe^{3+}, Fe^{4+} and Mn^{4+} implies a more than half filled Fe $e_{g\uparrow}$ band and an empty Mn $e_{g\uparrow}$ band. The Fe $e_{g\uparrow}$ band remains fully filled only if the Mn $e_{g\uparrow}$ band has charge carriers. This implies that the bottom of the Mn $e_{g\uparrow}$ band should be at the same level as, or higher than, the top of the Fe $e_{g\uparrow}$ band. Recently, Ahn *et al.*,[11] using the results of Banks and Tashima,[10] found that there is a slight overlap (less than 3%) between the $e_{g\uparrow}$ bands of Fe and Mn.

The nominal stoichiometry of our samples is $La^{3+}_{0.7}Sr^{2+}_{0.3}Mn^{4+}_{0.3}Mn^{3+}_{0.7-x}Fe^{3+}_x O_3$. The $t_{2g\uparrow}$ band of Fe and Mn and the $e_{g\uparrow}$ band of Fe are totally filled. There are $(0.7-x)$ electrons in Mn $e_{g\uparrow}$ band which has a capacity of two electrons, hence $(0.7-x)/2$ part of Mn $e_{g\uparrow}$ band is also filled. The width of Mn $e_{g\uparrow}$ is about 1 eV. So (assuming uniform filling of the band) the highest filled state in Mn $e_{g\uparrow}$ (Fermi level) will be $\approx (0.7-x)/2$ eV above the top of the Fe $e_{g\uparrow}$ band. In our system x lies between 0 and 0.25, so Fermi level will be about $\approx$0.3 eV above the top of the Fe $e_{g\uparrow}$ band. In an earlier report[15] it has been shown that in $LaFeO_3$ the Fe $t_{2g\downarrow}$ band lies about 2 eV above the top of the Fe $e_{g\uparrow}$ band. Assuming the same situation in our case, the Fe $t_{2g\downarrow}$ band will lie $\approx$1.7 eV above the Fermi level [see Fig 2(c)]. It is clear from this energy diagram that there are no states on Fe^{3+} which can participate in electron hopping from Mn. Consequently, the doping of Fe results in a depletion in the number of hopping electrons and available hopping sites and

hence weakens the double exchange interaction. This weakening causes the suppression of metallicity and the system is pushed towards the insulating side.

Although the simple band structure picture discussed above gives a qualitative account of the electrical conduction in the system, there are some issues which need further consideration. It is to be noted that, although for low Fe doping ($x \leqslant 0.2$) the material appears to be metallic [as far as the temperature coefficient of resistivity (TCR) is concerned] the magnitude of resistivity (ρ) is very high. These ρ values are larger than the Mott's maximum metallic resistivity[16] for the system, which is of the order of 1–10 mΩ cm. If we assume that each Mn^{4+} ion provides one hole, then with a molar volume $V \approx 36$ cm^3, charge carrier density is 10^{22}/cm^3. For this typical metallic carrier density a low conductivity value implies a low diffusivity for the carriers. Under such conditions charge carriers are expected to be strongly correlated. Furthermore, the electrical resistivity of these samples shows an upturn at low temperatures, a characteristic of disordered metallic systems. In strongly interacting disordered systems the density of states at the Fermi level is known to get modified. Altshuler and Aronov[17] have shown that $e-e$ interactions modify the density of states as: $N(E)=N(E_F)[1+(|E|/\Delta)^{0.5}]$, where Δ is a constant and $N(E_F)$ is the density of states at the Fermi level. So we felt that an investigation of the density of states near the Fermi level will be quite informative in understanding the nature of this system.

Tunneling conductance $G(V)=dI/dV$ of a metal-insulator-metal tunnel junction is a direct measure of the single particle density of states of the metal[18–20] at energy $E=q_eV$ from the Fermi energy, i.e., $G(V) \propto N(E+E_F)$. To investigate the density of states of $La_{0.7}Sr_{0.3}Mn_{1-x}Fe_xO_3$ near the Fermi energy we have performed electron tunneling experiments on $La_{0.7}Sr_{0.3}Mn_{1-x}Fe_xO_3$-insulator-Pb (superconductor) tunnel junctions. We chose Pb as the counter electrode and performed the measurements at 1.2 K where Pb is in the superconducting state. A superconducting material was chosen as the counter electrode because the observation of the superconducting energy gap is direct evidence of the quality of the tunnel junction and ensures that tunnel injection is indeed the form of charge transfer.[18] The superconducting correction to $G(V)$ is significant below $|V| \sim \Delta_{Pb}$; above this voltage range corrections are rather minor and the data can be interpreted as a direct measure of the density of states of the material.

Figure 3 shows the $G(V)$ vs V for all the samples in the range 10 mV$<|V|<$100 mV. We have normalized the tunneling conductance data of all the samples to unity at 100 mV and shifted them vertically for clarity. In all the cases a well defined superconductivity gap is observed. The inset of Fig. 3 shows the typical tunneling data of $La_{0.7}Sr_{0.3}MnO_3$ in the range $|V|<10$ mV, where a superconductivity gap is clearly seen.

All the metallic samples ($x \leqslant 0.2$) show a dip in the density of states near the Fermi energy. As the value of x increases the dip deepens. The tunneling conductance data of $x \leqslant 0.2$ samples follow the relation $G(V)=G_0[1+(|V|/\Delta)^n]$ with $n \approx 0.8-0.9$ (see Table I). This relation is very similar to that predicted by Altshuler and Aronov[17] for correlated

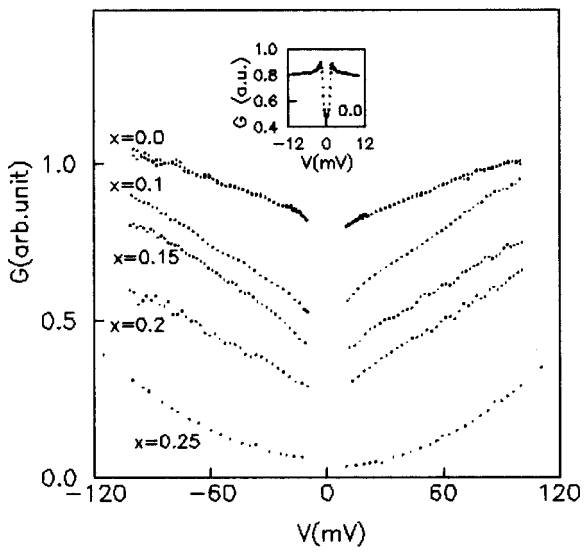

FIG. 3. Tunneling conductance $G(V)$ vs bias voltage for $La_{0.7}Sr_{0.3}Mn_{1-x}Fe_xO_3$ ($x \leqslant 0.25$) at 1.2 K. The data have been normalized to unity at 100 mV and shifted vertically for clarity. Information about the absolute values is given in Table I. Inset shows the superconductivity gap of Pb as seen in the low bias ($|V|<10$ mV) tunneling conductance data of $La_{0.7}Sr_{0.3}MnO_3$.

disordered metals except for the observed higher values of n. The value of n, predicted by them, is 0.5. These predictions are based on a perturbative approach, valid in the weakly disordered metallic regime. In the case of highly disordered metals the perturbative analysis may not be valid. There is no theory[21] which describes the $e-e$ interactions in the entire regime (weakly disordered metal, highly disordered critical regime and insulating regime). However, recent experimental results[22] have shown that as the disorder in the metallic system increases the square root dip in the density of states near the Fermi energy deepens and changes to a linear form for highly disordered systems in the critical regime and becomes a quadratic gap just on the insulating side. Therefore the values of n close to unity put these manganates ($x \leqslant 0.2$) into the class of highly disordered metals. Furthermore, as the value of x increases the value of n also increases, implying the increasing disorder in the system. Finally for $x=0.25$ a gap opens up at the Fermi level and tunneling data follow a parabolic dependence, a characteristic of insulating samples.

An interesting observation of this study is that even the parent compound $La_{0.7}Sr_{0.3}MnO_3$ is strongly disordered with electron correlation effects playing a crucial role. Disorder in the system is expected to arise because of the random potential fluctuations[3] seen by the conduction electrons due to the different electron negativities of La^{3+} and Sr^{2+}. Also, recent pulsed neutron diffraction experiments[23] have shown that the local atomic structure of $La_{1-y}Sr_yMnO_3$ is significantly different from the long range structure. Although the overall crystal structure suggests that the Jahn–Teller (JT) distortion is absent for $y>0.16$, the pair distribution function analysis[24] of neutron diffraction data shows that locally JT distortions are always present.[23] Doped charge carriers introduce local anti-JT distortions and disrupt the

long range JT distortion. In the paramagnetic phase ($T > T_c$), the anti-JT distortions localize the conduction band electrons as polarons. At low temperatures ($T < T_c$) the charge carriers are delocalized, but local lattice distortions are still present. These local lattice distortions may also contribute to the strongly disordered nature of the low temperature metallic phase.

When Fe is doped in the system it depletes the total number of conduction electrons and at the same time increases the randomness of the potential experienced by the remaining conduction electrons. For $x = 0.25$ the disorder becomes significant enough to cause a *M-I* transition and the material becomes insulating for $x \geqslant 0.25$.

IV. CONCLUSION

In summary we have done a systematic study of the electrical resistivity and electron tunneling conductance of $La_{0.7}Sr_{0.3}Mn_{1-x}Fe_xO_3$ ($x \leqslant 0.25$). The undoped material $La_{0.7}Sr_{0.3}MnO_3$ shows metallic behavior at low temperatures, however, this low temperature metallic phase is found to be highly disordered. As the concentration of Fe increases the number of hopping electrons decreases and the disorder increases, causing a tremendous increase in the resistivity of the system. For $x \geqslant 0.25$ the material becomes insulating throughout the whole temperature range.

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